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$(CH_3)_2OH^+ + e^- \rightarrow (CH_3)_2O + H$ **(1a)** $\Delta H^o_{298}(1a) \approx -509$ kJ mol^{-1}

$\rightarrow CH_3OH + CH_3$ **(1b)** $\Delta H^o_{298}(1b) \approx -597$ kJ mol^{-1}

$\rightarrow CH_3O + H + CH_3$ **(1c)** $\Delta H^o_{298}(1c) \approx -161$ kJ mol^{-1}

$\rightarrow CH_3 + O + CH_4$ **(1d)** $\Delta H^o_{298}(1d) \approx -222$ kJ mol^{-1}

$\rightarrow 2\ CH_3 + OH$ **(1e)** $\Delta H^o_{298}(1e) \approx -211$ kJ mol^{-1}

Thermochemical data for all the channels were taken from Ref. [1]. There are many more exoergic channels, but only the most plausible ones (those involving few rearrangements of the intermediate neutral) leading to very stable radicals were selected. All reactions (1a-d) are highly exoergic, so small errors (by different experimental methods or theoretical approaches) in the formation enthalpies cannot affect the viability of the processes.

Rate Coefficient Data *k*

k / cm^3 molecule^{-1} s^{-1}	T / K	Reference	Comments
Rate Coefficient Measurements			
$1.7 \times 10^{-6}(T/300)^{-0.70}$	20 - 1000	[1]	Storage ring
Rate Coefficient Reviews and Evaluations			
$3.0 \times 10^{-7}(T/300)^{-0.50}$	10 – 300	UMIST database	
$4.5 \times 10^{-7}(T/300)^{-0.50}$		OSU website	
Branching Fraction Measurements			
1(a) = 0.07 ± 0.05		[1]	Storage ring
1(b) = 0.49 ± 0.14			
1(c) = 0.00 ± 0.00			
1(d) = 0.00 ± 0.00			
1(e) = 0.44 ± 0.11			
Branching Fraction Reviews and Evaluations			
1(a) = 0.33	10 – 300	OSU website	
1(b) = 0.33			
1(c) = 0.00			
1(d) = 0.33			
1(e) = 0.00			
1(a) = 0.50	10 – 300	UMIST website	
1(b) = 0.50			
1(c) = 0.00			
1(d) = 0.00			
1(e) = 0.00			

Comments

The rate constants and the branching ratios of the dissociative recombination of the protonated dimethylether, $(CH_3)_2OH^+$ are deduced from those of the dissociative recombination of the fully deuterated $(CD_3)_2OD^+$ isotopomer studied using a storage ring experiment [1]. To the best of our knowledge this last is the only available indirect measurement of the overall rate and branching fractions of the title reaction. We also do not know of any theoretical study of this process

Preferred Values

Rate coefficient (10 – 1000 K):
$\boldsymbol{k}$ **(T) = 1.7 × 10^{-6}(T/300)$^{-0.77}$**

Reliability:
F_0 = 1.35 ; g = 0

Recommended branching fractions:
1(a) = 0.07
1(b) = 0.49
1(c) = 0.00
1(d) = 0.00
1(e) = 0.44

Comments on Preferred Values
In lack of other data, I recommend the branching fraction and rate constant from the storage ring experiment. Regarding the rate constant the problem could arise that the dissociative recombination of the deuterated isotopomer has in several compounds found to be slower due to less efficient tunneling processes caused by the lower zero-point energies of deuterated molecules. Interestingly, however, such a behaviour has not beenb observed in the related $CH_3OH_2^+$ system [2]. Also no large discrepancies of the product branching ratios has been detected between the light hydrogen and deuterium isotopomer for this ion. Thus we adopt the values obtained for $(CD_3)_2OD^+$ without any changes. The overall rate constant $(1.7\times10^{-6}(T/300)^{-0.70})$ appears reasonable for the system and is in line with other ions with such high mass. It seems to be a general trend for heavier ions to possess higher dissociative recombination rates.

The issue of the branching ratios is much more difficult. Many exoergic channels exist for the title reaction. Since the resolution of the ion-implanted silica detector was insufficient to elucidate the full branching ratios of all channels, only branching ratios between pathways leading to conservation of the COC chain and break-up into 2 or 3 heavy atom-containing fragments could be determined. Also it could be established that channels leading to the ejection of D_2 molecules or 2 or more deuterium atoms are not observed. It emerged that the carbon-oxygen chain stays intact in only 7 % of the dissociative recombination events. Channel 1(a) was regarded as solely responsible for these events since the other possible pathway producing only one deuterium atom (leading to methanol) involves large rearrangement of the system. 49 % of the dissociative recombination reactions lead to break-up into two heavy fragments and were attributed to channel 1(b), since the proceess analogue to reaction 1(d) leading to CH_3O + 2H was not observed in the dissociative recombination of $CH_3OH_2^+$. Finally, 44% of dissociative recombination processes of protonated dimethyl ether involves break up of both C-O bonds. They are regarded as being due to channel 1(e).

References

[1] M. Hamberg, F. Österdahl, R. D. Thomas, V. Zhaunerchyk, E. Vigren, M. Kaminska, M. af Ugglas, A. Källberg, A. Simonsson, A. Paál, M. Larsson, and W. D. Geppert, Astron. Astrophys. **514,** A83 (2010)
[2] W. D.Geppert, M. Hamberg, , R. D. Thomas, et al. Faraday Discuss. **133,** 177 (2006)

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